Investigation of the removal of heavy hazardous metals by agricultural solid waste as an cheap reliable adsorbent

Maryam K Hafshejani[1], Ameneh Langari[2], Mehdi Khazaei[3*]

[1] Shahrekord University of Medical Sciences, Shahrekord, Iran
[2] North Khorasan University of Medical Sciences, Bojnurd, Iran
[3] Bushehr University of Medical Sciences, Bushehr, Iran
[*]Email: researcher2280@yahoo.com

Abstract: It is well-recognized that the heavy metals are among the prominent contaminants in aqueous solutions. This hazardous metal can result in a high risk contamination and causes illness. It should be mentioned that the metals also appears in wastewaters of a lot of manufacture and it can produce variety of undesirable effects. For removal of this contaminant from water many methods are used in this way. This paper investigates adsorption Sr (II) from aqueous solutions is the most important aim of this paper. A low cost adsorbent which prepared by hazelnut shell as an agricultural solid waste was used in this study. The best of our knowledge is to use solid waste as an adsorbent without converting it to activated carbon, just by simple method. Some operational conditions such as temperature, speed velocity of stirrer and dose of prepared adsorbent were investigated by some experiments. The high efficiency adsorption was achieved by this low cost adsorbent. The raw material in this research was collected from Iranian garden.

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1. Introduction

It is well recognized that with recent development in industrial activities, contaminants are become one of the major problems especially in developed countries as well as third world countries. Therefore, the removal of contaminants is one of the most important problems for health and medical science as well as engineering. Heavy metals are among the prominent contaminants in aqueous solutions. This hazardous metal can result in a high risk contamination and causes illness. It should be mentioned that the metal also appears in wastewaters of a lot of manufacture and it can produce variety of undesirable effects like nausea, vomiting, asthma, damage to heart, causing heart failure, damage to thyroid and liver on human beings[1-2].

For removal of this contaminant from water many methods are used in this way. Some nanoparticles such as ZnO can be used for contaminant degradation [3-5]. Human activities, such as the discharge of industrial wastes and mining operations, have resulted in the accumulation of metals in the environment [1].

Some metals such as Ca, Co, Cr, Cu, Zn, Fe, K, Mg, Mn, Na and Ni are essential micro-nutrients for most living organisms. One of the most important functions of the micro-nutrients is their role in metalloenzymes. However, when the concentrations of the beneficial metals, for instance, the copper or the zinc in the environment are excessively high they can become toxic to these microorganisms and human [2,6]. The uptake of heavy metal ions from wastewater has attracted a great attention in recent years for global awareness of the underlying detriment of toxic metals in the environment. Application of traditional processes for the uptake of heavy metals has enormous cost, and they cause further environment damage because of the continuous input of chemicals.

Hence, easy, effective, economic and ecofriendly techniques are required for fine-tuning of effluent wastewater treatment. Biosorption of metals by biomass has been much explored in recent years. Different form of inexpensive, non-living plant material such as rice husk [7], sawdust [8] and pine bark and canola meal [9-11] have been widely investigated as potential adsorbents for the mentioned heavy metals.

In recent years, adsorption techniques have been widely investigated for the removal of heavy metals from wastewaters. Adsorbent used in the adsorption processes are various materials including activated carbons prepared from some agricultural by-products, some cellulosic wastes and their carbonization products, bituminous coal and commercial activated carbons [12].

However, the high cost of the activation process limits the use in wastewater treatment, particularly for the needs of developing countries. Therefore, over the last few years numbers of investigations have been conducted to test the low-cost adsorbents for heavy metal ion removal.

Table. 1. Characterization of Hazelnut Shell.

Material	Hazelnut Shell
Basic groups	0.52
Carboxylic groups	0.45
Lactonic groups	0.49
Phenolic groups	0.39
Total acidic groups	1.33
Surface Area (m^2/g)	890

It should be noted that in this paper the main aim is to use agricultural solid waste as a low cost adsorbent for removing these dangerous contaminants. The important point in this study is to use hazelnut shell as an adsorbent without preparing activated carbon by this raw material. Some operating conditions such as speed velocity of stirrer, temperature, dose of adsorbent. Hazelnut shell has been purchased from Ghazvin city in Iran. The local hazelnut shell was characterized in Table. 1. The prominent point in this research is to prepare hazelnut shell for adsorption just by some simple operations on it. Sr (II) was selected as a contaminant for this present research.

The disposal of radioactive wastewater from commercial nuclear plants is one of the major problems in nuclear waste management. Some of the important isotopes in the radioactive wastewaters are strontium, cesium, plutonium, americium and technetium [13]. 90Sr is one of the products of nuclear fission in radioactive waste effluents resulting from reprocessing of nuclear fuels. Furthermore, strontium has a variety of commercial uses. It is used in certain optical materials and produces the red flame color of pyrotechnic devices such as fireworks and signal flares. Due to the long life, high solubility, and bio-toxicity of strontium, separation and recovery of this ion from waste solutions needs special attention. During the last decades, researchers have put numerous efforts to develop suitable processes for better separation of radioactive ions from wastewater.

2. Materials

In this research work, all of the chemicals and reagents used were of analytical grade supplied by E-Merck India. For using the hazelnut shell as an adsorbent some activities must have been done. First the local hazelnut shell collected and dried.

The temperature for drying the shell is 110 oC. After drying, sieving the dried shell was carried out. Mesh No. 110 was used for achieving the homogenous particle. For putting the various functional group on the shell, the ammonia and oxygen peroxide have been purchased. 2% volume has been selected of the oxygen peroxide and ammonia for appropriate impregnation. After completing the impregnation process of adsorbent, the black achieved material was dried again in 100 C.

3. Adsorption Study

The adsorption of Sr (II) from industrial leachate onto hazelnut shell was performed using the batch equilibrium technique.

It should be noted that all batch experiments were conducted with adsorbent samples with 500 mL. To obtain the optimum conditions of pH, adsorbent dosage, contact time and temperature, Erlenmeyer flasks with glass stoppers in a thermostated shaking water bath were used.

Batch experiments were carried out in a pH 5 were conducted in a Mettler Toledo MP 220 pH meter using 0.1 M HC solution. To determine the effect of adsorbent dosage, various adsorbent dosages ranging from 0.2 to 1.5g were introduced into 500 mL flasks with 50 mL solution. The flasks were then placed in an orbital shaker and agitated up to a total contact time of 120 min at fixed agitation speed of 200 to 700 rpm. Samples were taken at predetermined time intervals (5, 10, 20, 40, 60, 90 and 120 min) and then separated by the filtration process.

To determine the effect of temperature on the adsorption of Sr (II), experiments were also conducted at 30, 40, 50 and 60 ◦C. Sr (II) concentrations of aqueous phases were analyzed by atomic absorption spectrometric procedure using a flame atomic absorption spectrophotometer (UNICAM model 929) with an air–acetylene flame and a hollow cathode lamp. Each experiment was performed in duplicate to observe the reproducibility and the mean value used for each set of values.

3. Adsorbent Characterization:

Textural characteristics of samples were determined by nitrogen (N2) adsorption at −196 ◦C with ASAP-1100, micromesetics. The specific surface areawascalculated from the isotherms by using the Brunauer–Emmett–Teller (BET) equation. The pore volume was found from the amount of N2 adsorbed at a relative pressure of 0.99. Sharp increase of the adsorbed volume at low pressure is due to the enhanced potential of micropores, and gradual increase at higher pressures indicates the presence of mesopores in the sample. The average pore diameter was calculated from four times of the pore volume over the BET surface area. The types and amounts of surface functional groups that present in the adsorbent were determined by the Boehm Analysis and the obtained results are seen in Table. 1.

4. Results and Discussions:

4.1. The speed velocity of stirrer:

For determination of effect of speed velocity of stirrer the all conditions such as temperature, Dose and initial concentrations of experiments have been fixed. Just the speed velocity of set up has been changed in range of 200 to 700 rpm. As shown in Fig .1. the curve of these results has one maximum pick on 600 rpm. With increasing the speed velocity of stirrer the adsorption efficiency has been increased but after the 600 rpm the efficiency has been decreased. Efficiency of Sr (II) adsorption is reached by equation 1.

$$R = \frac{(C_0 - C)}{C} \times 100 \qquad (1)$$

Where R is the removal efficiency of adsorbent, C0 and C are the initial and equilibrium concentrations of metal ion (ppm) in the aqueous solution. (The initial concentration= 50 ppm, temperature = 30°C, pH= 5 and dose=0.75g).

5-2- Dose of adsorbent:

Clearly, with increasing the dose of adsorbent in adsorption process the efficiency and adsorption capacity will be increased but the minimum dose which has the maximum efficiency must be determined. For calculation the maximum efficiency and find its relation with dose, equation 1 has been used. The results have been depicted in Fig. 2. The best dose is 0.75g because of in this amount of adsorbent the efficiency of adsorption has been stable. The initial concentration= 50 ppm, temperature = 30°C, pH= 5 and speed velocity of agitation =600rpm were fixed.

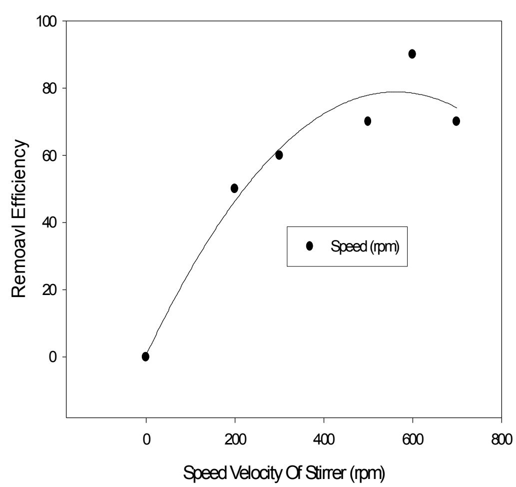

Fig. 1. Speed Velocity of Stirrer (rpm) Effect

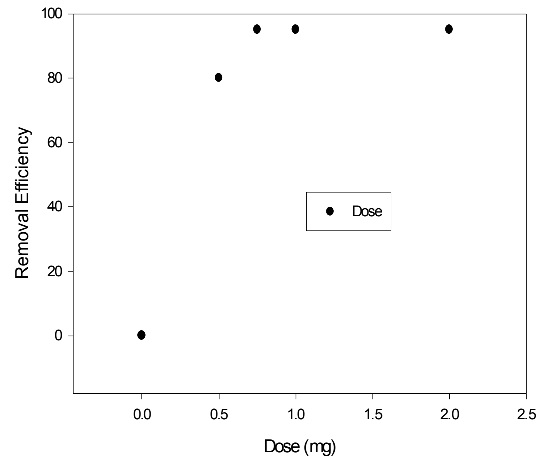

Fig. 2. Dose Effect

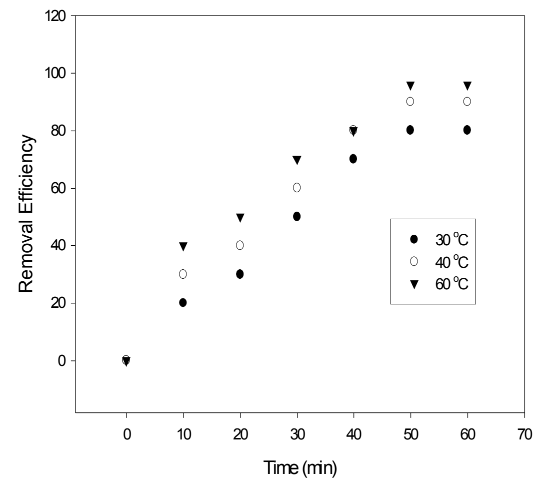

Fig. 3. Temperature Effect

5-3- Temperature influence on Sr (II) adsorption:

Temperature is the main factor in the adsorption process. This parameter can be affected on the one of the adsorption process steps such as diffusion from bulk, diffusion from interface, putting on the adsorbent surface, diffusion from porosity if adsorbent and physical Vander –Waals. In this study it is clear that with increasing the temperature the adsorption temperature is increased in the selected temperature range. It is shown that the diffusion step is the determination step for the process. The results are shown in Fig. 3. For testing the temperature effect, another operation conditions must be fixed. (The initial concentration= 50 ppm, speed velocity=600 rpm, pH= 5 and dose=0.75g).

But it should be said that with increasing the temperature over 60°C, the efficiency will be decreased. In some industries the wastewater temperature is in this range which is tested in this study.

4. Conclusion:

In this paper, the high light of our study is to use agricultural solid waste as a low cost adsorbent for removal of heavy metals such as Sr (II) ions from aqueous solutions. The local Iranian hazelnut shell uses as an adsorbent without converting it to activated carbons. Just by some titration with ammonia and oxygen peroxide the suitable adsorbent will be achieved for adsorption of Sr (II). Some operational conditions such as speed velocity of stirrer, temperature and dose of adsorbent have been tested and investigated in similar conditions. It is clear from the manuscript of paper that increasing the temperature in range of 30 to 60^{o}C can increase the efficiency of adsorption. Speed velocity of stirrer in range of 200 to 700 rpm also has been checked by some useful experiments. It is clear from results which were depicted in this research that with increasing the speed velocity the efficiency of adsorption will be increased but until 600 rpm. Over the 600 rpm the diverse effect will be done. The best amount of adsorbent is 0.75g for 50 mL solution.

Corresponding Author:
Dr. Mehdi Khazaei
Bushehr University of Medical Sciences, Bushehr, Iran
Email: researcher2280@yahoo.com

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